

# Model Predictions and Field Measurements of Chlorsulfuron Leaching under Non-steady-state Flow Conditions

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**Abstract:** Model simulations of chlorsulfuron (1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea) leaching in a loamy soil were made with the mechanistic dual-porosity model MACRO. Comparisons were made with a data set obtained in a lysimeter experiment in which leaching was measured during an 11-month period after applying chlorsulfuron at two rates (4 and 8 g ha<sup>-1</sup>). In this experiment, peak concentrations appeared c.6 months after pesticide application, reaching levels of 14 and 21 ng litre<sup>-1</sup> in the low- and high-dose treatments, respectively. These peak concentrations appeared after c.70 mm of accumulated leachate, implying that some of the herbicide was displaced through the soil columns by non-equilibrium flow processes. Model calibration was limited to parameters related to evapotranspiration, water uptake by roots and degradation rates in the subsoil. With this minimum amount of calibration, the model successfully described the leaching pattern of chlorsulfuron, provided that the two-flow domain option in the model was used. Running the model in one-flow domain resulted in considerable underestimates of leaching of chlorsulfuron over the short-term (<1 year). The degradation rate in the subsoil was also found to be critical. It had to be increased about fivefold to match measured chlorsulfuron concentrations in leachate. At such concentrations, 0.012 g ha<sup>-1</sup> of chlorsulfuron (0.3% of that applied) was predicted to leach through the soil profile during the 11-month simulation period when the lower dose of the compound was applied.

**Key words:** chlorsulfuron, degradation rate, leaching, lysimeters, model predictions, preferential flow

## 1 INTRODUCTION

Transport of agricultural chemicals through soils has become a problem of international concern, due to its potential for causing deterioration in surface water and groundwater quality. Although the concentrations in these environments are usually very low and typically below levels of toxicological concern,<sup>1</sup> a significant number of pesticides have been detected.<sup>1–3</sup> These are often attributed to leaching through the unsaturated zone.

In addition to direct measurements, mathematical simulation models are now increasingly being used to predict pesticide transport in soil. Models provide a relatively inexpensive way of estimating likely leaching

behaviour for a variety of environmental conditions, which would not be feasible with costly field studies. Accordingly, several simulation models are now available for prediction of pesticide fate in soil, ranging in scope from simple functional models with limited data requirements to comprehensive mechanistic models (see review by Jarvis *et al.*).<sup>4</sup> One limitation for extensive use of detailed mechanistic models is the difficulty in determining appropriate parameter values. Another restriction for extensive model use is the fact that our current understanding of the basic mechanisms of pesticide transport and transformations in the unsaturated zone is sometimes insufficient to predict the occurrence or lack of occurrence of the very low pesticide levels often detected in water.<sup>5</sup> Also, the environmental fate of

pesticides in soil is a reflection of many interacting processes occurring in a complex soil structure under non-steady-state conditions. For example, preferential-flow behaviour, which is mostly ignored in pesticide leaching models due to its complexity, may explain the presence of trace levels of pesticide deep in the soil profile and in surface waters soon after application. Oversimplified model descriptions of the mechanisms behind sorption/desorption and degradation of pesticides are other examples of factors that may contribute to poor agreement between measurements and predictions.<sup>6,7</sup> Nevertheless, simulation models may have great potential as prediction and evaluation tools (as shown in this paper).

The objective of this study was to test the ability of the mechanistic model MACRO,<sup>8</sup> to predict, with a minimum of calibration, very low concentrations of pesticides in leachate. Predictions were compared with the results of a leaching study performed in field lysimeters with the low-dose herbicide chlorsulfuron (1-(2-chlorophenylsulfonyl)-3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea). The reasons for choosing MACRO for this exercise were the possibility of evaluating non-equilibrium flow behaviour, something that the measurements suggested was occurring, and its documented good ability to reproduce pesticide leaching results obtained in lysimeters.<sup>9</sup>

## 2 MATERIALS AND METHODS

### 2.1 Description of leaching experiment

Two undisturbed soil monoliths (0.3 m diameter and 0.7 m deep) were used to study leaching of chlorsulfuron. The soil profile was characterized by a moderately aggregated loamy topsoil layer down to c.0.3 m depth, overlying a more or less structureless loamy fine sand layer down to a depth of c.0.7 m. Some physical and chemical properties of this soil are listed in Table 1. The monoliths were taken out with a coring technique in which a standard PVC sewer pipe (0.3 m diam., 1.18 m depth) was gently pressed into the soil by a steel cylinder, equipped with four mounted cutting teeth, which rotated around the pipe as it penetrated the soil.<sup>10</sup> After collection, the monoliths were placed below ground in the same field as they were collected, at Kjettslinge in

central Sweden (60°10'N, 17°38'E), and leaching was followed during an 11-month period.

On 3 June 1988, chlorsulfuron 200 g kg<sup>-1</sup> WG ('Glean' 20 DF; du Pont) was applied at two rates, 4 and 8 g AI ha<sup>-1</sup>, in single applications in a spray volume of 250 litre ha<sup>-1</sup>. The compound was applied in a spring barley crop (*Hordeum distichum* L.), which was sown on 6 May and harvested on 5 September 1988. In addition to natural precipitation, the lysimeters received supplemental irrigation on eight occasions at rates of 6 to 25 mm per day, totaling 141 mm.

Three days prior to chlorsulfuron application (31 May 1988), the monoliths were wetted until leachate was observed at the lysimeter bottoms. This was done to ensure that the initial water content in the two monoliths was the same and close to field capacity.

Water draining through the monoliths was collected weekly if leachate was available and subsamples were analysed for chlorsulfuron concentration by ELISA (Enzyme-Linked Immunosorbent Assay) microplate immunoassay<sup>11</sup> at The Battelle Institute E.V. in Frankfurt, Germany, in compliance with the OECD Good Laboratory Practice Guidelines. All of the water samples were immediately put into the assay as they were received at the laboratory, starting with incubation together with buffers, protein blockers and calcium chloride, and with a dilution of antisera typical of chlorsulfuron. Using antigen-coated microwell plates, the concentration of remaining unbound antibody in the samples was measured. This level should be inversely proportional to the chlorsulfuron concentration of the original sample. These measurement values were then compared with those of standards made up in untreated water. The detection limit was 12.5 ng litre<sup>-1</sup>.

A more detailed description of the experimental setup and analytical procedures, and results from the first seven-month period (until 31 December 1988) are given elsewhere.<sup>12</sup>

### 2.2 Model description

MACRO is a comprehensive environmental fate model which simulates the field water balance, solute transport and transformation processes of pesticides in the soil/crop system. Version 3.1 of the model, which was used

TABLE 1  
Selected Soil Properties of the Kjettslinge Monoliths

Layer	Particle size distr. <sup>a</sup> (%)	Organic matter (%)	pH	Bulk density (g cm <sup>-3</sup> )	Water content at tensions (cm)		
					0	100	15 000
					(m <sup>3</sup> m <sup>-3</sup> )		
Topsoil	20/14/66	4.5	6.5	1.45	0.45	0.38	0.15
Subsoil	5/4/91	1.0	5.7	1.60	0.40	0.23	0.05

<sup>a</sup> Clay/Silt/Sand.

in this study, is described in detail by Jarvis<sup>8</sup> and only a brief overview of the model structure is presented here.

### 2.2.1 Water balance

The model uses standard meteorological data as driving variables (i.e. precipitation, maximum and minimum air temperatures and potential evapotranspiration). Rainfall added to the canopy in excess of the sum of daily evaporation loss and the interception capacity becomes throughfall. The partitioning between the amount of pesticide stored on the canopy and that washed off to the soil surface is calculated according to simple sub-routines in the PRZM model.<sup>13</sup>

An important feature of the model is that it may be run in either one or two flow domains with no change in the hydraulic properties assumed to characterize the soil. In the two domains, the total porosity is partitioned at a boundary water content/potential into macropores and micropores. Water movement in the micropores is calculated with the Richards' equation, including a sink term to account for root water uptake. The soil hydraulic properties are described by the functions of Brooks and Corey<sup>14</sup> and Mualem.<sup>15</sup> Water flow in macropores is calculated with Darcy's law assuming a unit hydraulic gradient and a simple power law function to represent the unsaturated hydraulic conductivity. Mass exchange between the two flow domains is calculated using approximate, but physically based, expressions based on an effective aggregate half-width.

The surface boundary condition in MACRO partitions the net rainfall into an amount taken up by micropores and an excess amount of water flowing into macropores. Alternative options for the bottom boundary condition are available in the model (i.e. constant hydraulic gradient, zero flux, constant potential with or without inflow of water at the bottom boundary).

Root water uptake is predicted as a function of the evaporative demand, root distribution and soil water content using a simple empirical model described by Jarvis.<sup>16</sup> The calculated water uptake is assumed to be preferentially satisfied from the water stored in the macropores.

### 2.2.2 Pesticide transport and transformations

Transport is predicted using the convection-dispersion equation for a sorbing solute subjected to plant uptake and degradation. As in earlier two-domain approaches,<sup>17</sup> the sorption sites are assumed to be partitioned into one fraction that equilibrates with the macropore fluid and another fraction that equilibrates with the micropore liquid. Also, an instantaneous equilibrium between solution and sorbed phases and a linear sorption isotherm are assumed.

Pesticide uptake is modelled as a function of the water uptake, the concentration in the liquid phase and

a 'concentration factor' varying from zero to unity (i.e. passive uptake).<sup>18</sup>

Degradation is predicted assuming first-order kinetics. Four separate reference degradation rate coefficients may be specified in the model since the pesticide may be stored in the two phases and in the two flow domains.<sup>17</sup> Field degradation rate coefficients are predicted from the laboratory-measured reference values accounting for soil moisture and temperature effects using simple functions.<sup>18</sup> Soil temperatures are calculated from air temperatures using the heat conduction equation. The top boundary condition is given as the soil surface temperature approximated by a sinusoidal diurnal variation in air temperature while the bottom boundary condition is predicted from an analytical solution of the heat conduction equation assuming a sinusoidal variation of temperature at the soil surface on an annual basis.

Solute transport and transformation processes are treated in the same way in micropores and macropores, except that dispersion is neglected in the macropores where convection is assumed to dominate.

## 2.3 Model application

Several of the input parameters required by MACRO were available for the Kjettslinge soil.<sup>19</sup> Accordingly, calibration was limited to obtaining reasonable values of non-measurable parameters and parameters for which site-specific measurements were not available. Appropriate estimates of many such parameters could be obtained from previous experience with the model.<sup>9</sup> The procedure followed was first to calibrate the model against measured leachate volumes by varying parameters related to evapotranspiration and water uptake by roots. Subsequently, typical literature values for pesticide parameters were used to test the ability of the model to simulate observed leaching of chlorsulfuron applied at the lower application rate ( $4 \text{ g ha}^{-1}$ ). This was done without model calibration and with the model run in both one- and two-flow domains. Calibration was then attempted to achieve a better fit to measured data, concentrating solely on changing the degradation rate in subsoil. Chlorsulfuron leaching at the higher application rate ( $8 \text{ g ha}^{-1}$ ) was then simulated without additional calibration.

In all the model runs described here, a bottom boundary condition suitable for lysimeter experiments was used (i.e. zero water potential but with no inflow of water). The initial water content in the profile was assumed to be in drainage equilibrium with a water table at the base of the soil monolith (0.7 m depth), three months prior to application of chlorsulfuron.

In addition to simulations covering the period for which comparison with measurements was possible (June 1988–April 1989), model predictions were also

made for 44 additional months, until 31 December 1992.

### 2.3.1 Parameter estimation

To provide adequate numerical accuracy, the 0.7-m deep soil profile was divided into 11 layers with thicknesses varying between 0.02 and 0.08 m. However, only two horizons (0–0.3 and 0.3–0.7 m) were identified as having different properties; these are referred to as topsoil and subsoil. As indicated above, most of the parameter values of soil hydraulic properties were based on site-specific measurements. These are presented in Table 2. However, some soil hydraulic parameters were set to default values supplied with the model because no information was available from the field site; e.g. the effective aggregate half-width was fixed at 20 mm. Parameters related to root water uptake were adapted to obtain a good agreement with measured leachate volumes. A reasonable fit was achieved by assuming 60% of the total root length present in the top 10 cm of the soil profile (*cf.* Hansson *et al.*)<sup>20</sup> and with optimal uptake rates maintained to water tensions of 2 m. The maximum root depth was fixed at 0.4 m, in accordance with field measurements.<sup>20</sup>

Since no measurements of chlorsulfuron degradation and sorption were available for the Kjettslinge soil, typical values of these pesticide properties were first tested, i.e. sorption coefficients ( $K_d$ ) of 1.04 (topsoil) and 0.23 (subsoil)  $\text{cm}^3 \text{g}^{-1}$  (corresponding to  $K_{oc} = 40 \text{ cm}^3 \text{g}^{-1}$ ), and a degradation rate coefficient of  $0.014 \text{ day}^{-1}$  (corresponding to  $t_{1/2} = 49$  days) for the whole profile. Using these values for the pesticide parameters, the model considerably overestimated the measured concentrations of chlorsulfuron in leachate when the two-flow domain option was used. Therefore, faster degradation in the subsoil was assumed (i.e. a degradation rate coefficient of  $0.07 \text{ day}^{-1}$ ). The degradation rate was assumed to be the same in both phases and in both flow domains. The  $K_d$  values were obtained from  $K_{oc}$  estimates by assuming that sorption is proportional to organic matter content in the different layers.

When the model is run in two flow domains, the fraction of sorption sites assumed in the macropore system is critical. This parameter was, for the sake of simplicity, fixed at 0.1 in all simulations, which, on average, would result in a similar retardation factor for pesticide transport in both pore systems.

Solute transport parameters in all simulations (e.g. dispersivity) were set to default values supplied with the model.

Based on observations when spraying the monoliths on 3 June 1988, 35% of the applied herbicide was assumed to be intercepted by the plant canopy in all model runs. As in earlier MACRO simulations,<sup>9</sup> the extraction coefficient for canopy washoff was set to  $0.10 \text{ cm}^{-1}$ , while the canopy degradation rate coefficient (a lumped parameter including effects of volatilization, photodecomposition, etc.) was set to  $0.2 \text{ day}^{-1}$ . An empirical exponent describing the effects of soil water conditions on degradation was set to 0.7 in all cases.<sup>18</sup> No uptake of chlorsulfuron by the crop was assumed.

### 2.3.2 Driving variables

On-site measurements (from 1 March 1988 to 30 April 1989) of daily precipitation and daily maximum and minimum air temperature (Fig. 1), and calculated potential evapotranspiration (Penmans' equation) from the Kjettslinge field site in central Sweden were used as weather input. A mean rainfall intensity of  $2 \text{ mm h}^{-1}$  was assumed, which is the default value provided by the model. Observations at the site suggest that this is a reasonable value (Bergström, L., unpublished). For simulations extending beyond the leaching measurement period, weather conditions were assumed to be the same each year as during the first year.

Winter periods with freezing and snow are difficult to handle in the model since water and heat flow are not treated as coupled processes. Therefore, the precipitation data files were adjusted for the winter periods by simply setting the precipitation to zero during the period 20 November to 28 February of the following

TABLE 2  
Input Parameters in the Model: Soil hydraulic Properties

	Depth (cm)	$K_s$ ( $\text{mm h}^{-1}$ )	$K_b$ ( $\text{mm h}^{-1}$ )	$\psi_b$ (cm)	$\theta_s$ ( $\text{m}^3 \text{m}^{-3}$ )	$\theta_b$ ( $\text{m}^3 \text{m}^{-3}$ )	$\lambda$
Topsoil	0–30	155	0.06	10	0.45	0.43	0.15
Subsoil	30–70	100	2.5	10	0.40	0.38	0.5

Parameter symbols:

- $K_s$  total saturated hydraulic conductivity
- $K_b$  saturated hydraulic conductivity of soil micropores
- $\psi_b$  boundary tension between macropores and micropores
- $\theta_s$  saturated water content
- $\theta_b$  water content at  $\psi_b$
- $\lambda$  pore size distribution index

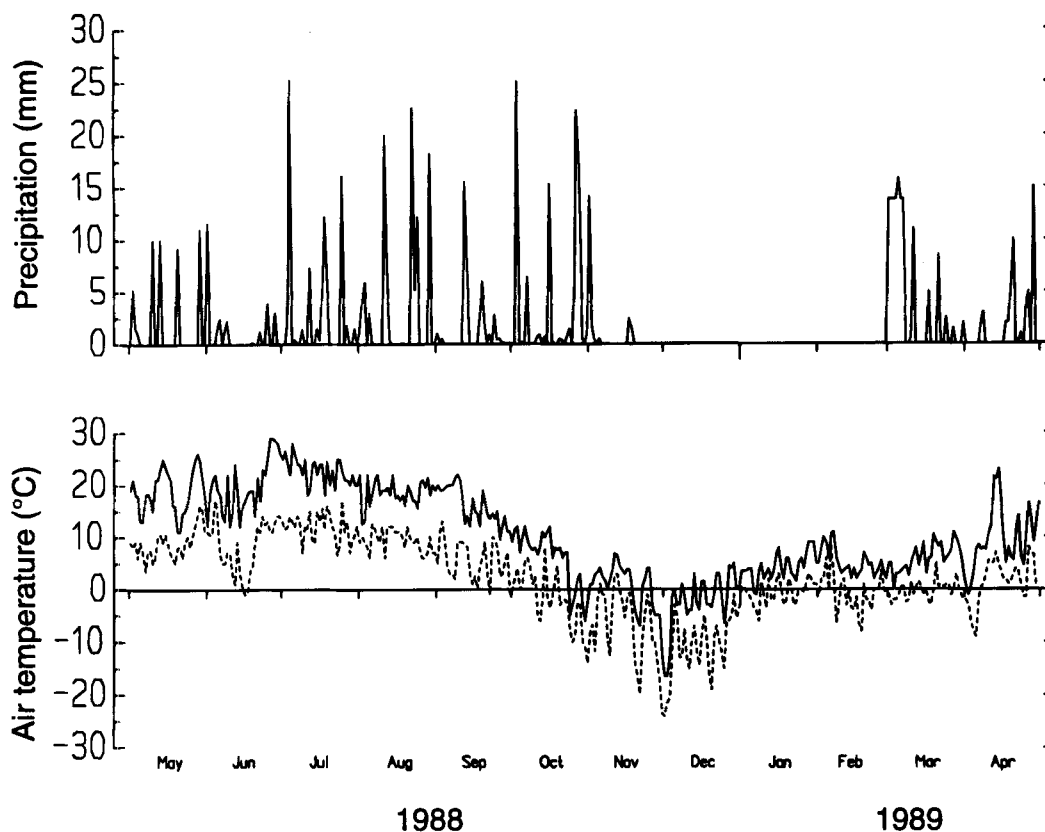


Fig. 1. Daily precipitation and daily maximum (solid line) and minimum (broken line) air temperatures at the Kjettslinge site. Precipitation is presented as it was used in the simulations (i.e. including irrigation and the break during winter).

year. The accumulated amount of precipitation during this period (96 mm) was then added to the soil over a period of one week (divided into equal daily amounts), when average air temperatures remained consistently above freezing.

### 3 RESULTS AND DISCUSSION

#### 3.1 Drainage conditions and soil water balance

As is typical of Swedish climatic conditions, two main drain-flow periods were predicted: in late autumn/early winter before soil freezing and in late winter/early spring in response to soil thawing (Fig. 2). The start of the second drainage period was determined by the date on which snowmelt was assumed to occur. Measurements showed breakthrough of water in autumn a few weeks earlier than suggested by the predictions (Fig. 2). This was presumably due to an inaccurate assumption of the initial moisture status in the soil profile. In the simulations, drainage equilibrium with a water table at 0.7 m depth was assumed to be present at the beginning of March 1988, whereas leachate was collected in each monolith as late as 31 May 1988 as a result of watering. Once the monoliths were wetted up to field capacity in late autumn, reasonable agreement between measured and predicted drain-flow patterns was obtained (Fig. 2).

Comparing drainage patterns of the two different flow-domain options, the two-domain simulation corresponded best with the measurements, both in terms of an earlier breakthrough of water in autumn and also considering the total amounts of leachate (Fig. 2). Over the whole period after chlorsulfuron application (1 June 1988–30 April 1989), the total amounts of leachate were 138 and 169 mm in the one- and two-flow domain simulations, respectively, as compared with the measured average value of 156 mm. These amounts are

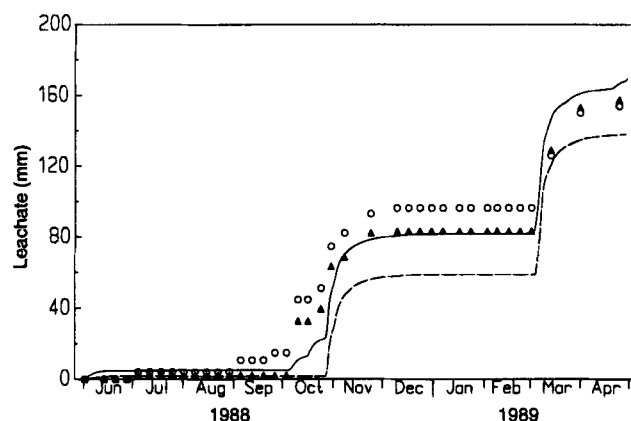


Fig. 2. Model predictions (lines) and measurements (dots) of cumulative leachate. The solid line refers to the two-flow domain simulation and the broken line to the one-flow domain simulation.

equivalent to 25–30% of the total water inputs (precipitation + irrigation) to the soil, which corresponds very well with the portion of rainfall that is typically recovered as leachate under Swedish conditions.<sup>21</sup>

The predicted soil water balances showed small increases in water storage of the profiles (12 and 8 mm in the one- and two-flow domain approaches, respectively) during the 11-month period. This was based on a total water input of 548 mm, leachate amounts of 138 and 169 mm, and predicted evapotranspiration losses of 398 mm (one-flow domain simulation) and 371 mm (two-flow domain simulation). No water losses through surface run-off were predicted, which corresponds with the situation in the lysimeters. The evapotranspiration values are slightly larger than previous estimates of actual evapotranspiration for spring-sown barley in the Uppsala region.<sup>22</sup> Jarvis *et al.*<sup>9</sup> explained this in terms of increased evaporation rates from irrigated lysimeters due to advection effects caused by dry surfaces surrounding the lysimeters. A similar explanation was given by Boesten.<sup>23</sup> However, in this study, the lysimeters were surrounded by vegetation, which presumably reduced such advection effects to a minimum.

### 3.2 Chlorsulfuron concentrations in leachate

When using typical values for pesticide parameters, the lower application rate ( $4 \text{ g ha}^{-1}$ ) and the one-flow domain option, the model completely failed to match measured chlorsulfuron concentrations in leachate (Fig. 3). The measured peak in November 1988 was not predicted to occur and the concentrations the following spring were much lower than the measurements indicated. In the subsequent model run using the two-flow domain approach (Fig. 3), an early breakthrough of chlorsulfuron in autumn was now apparent, although at

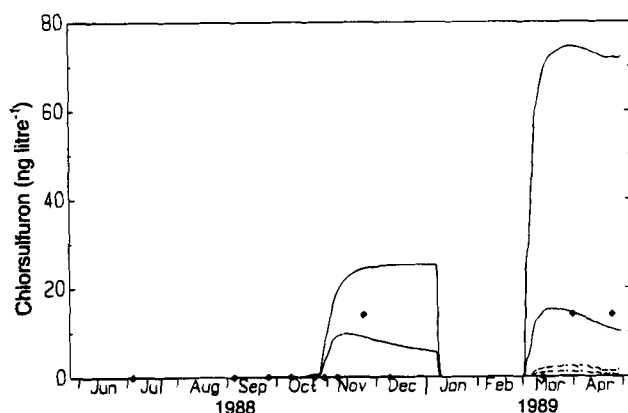


Fig. 3. Measured (dots) and predicted (lines) chlorsulfuron concentrations in leachate after applying the herbicide at  $4 \text{ g ha}^{-1}$ . The solid lines refer to the two-flow domain simulations and the broken lines to the one-flow domain simulations, of which the upper and lower curves of each flow-domain option are representative of slow and fast subsoil degradation, respectively.

a somewhat higher level than was measured. The measured spring peak was also considerably overestimated by the model. Good agreement between prediction and measurements was obtained after adjusting the degradation rate in the subsoil from  $0.014$  to  $0.07 \text{ day}^{-1}$ , and with the model still run in two-flow domains (Fig. 3). The faster degradation assumed in subsoil can be justified by the lower pH than that in the topsoil (Table 1). Hydrolysis is a significant degradation mechanism for chlorsulfuron, with shorter half-lives expected in soils of lower pH.<sup>24</sup>

The calculated concentrations were more or less directly proportional to the pesticide use rate, so that the predicted concentrations for the  $8 \text{ g ha}^{-1}$  application were simply twice as large as those of the  $4 \text{ g ha}^{-1}$  application (Fig. 4). Thus, two concentration peaks were also predicted in response to drain-flow periods in the double-dose simulation, provided that the two-flow domain option was used (Fig. 4). The first peak in autumn 1988 matched the measured concentrations quite well. However, the predicted concentration peak in spring 1989, which reached  $c.30 \text{ ng litre}^{-1}$ , was not representative of the measurements. After falling to a non-detectable level in December 1988, the measured chlorsulfuron concentrations remained below the detection limit during the subsequent spring in the double-dose treatment (Fig. 4). A distinct chlorsulfuron peak was predicted to occur in leachate during the spring period ( $c.10$  months after application) even when the degradation rate coefficients in the subsoil were set to values  $>0.07 \text{ day}^{-1}$  (equivalent to half-lives  $<10$  days). The most likely explanation for the failure of the model to reproduce this observed rapid concentration decrease is the use of inappropriate degradation rate coefficients in the simulations. It is quite likely that typical degradation rates for chlorsulfuron determined in the laboratory are not representative of conditions in the lysimeters, such that field degradation rates were significantly larger in the topsoil than those assumed. Also,

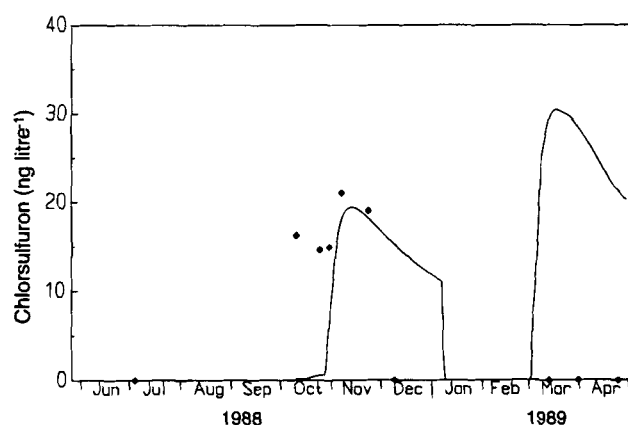


Fig. 4. Measured (dots) and predicted (line) chlorsulfuron concentrations in leachate after applying the herbicide at  $8 \text{ g ha}^{-1}$ , using the two-flow domain option and assuming fast subsoil degradation.

there may have been a failure of the simple response functions to account for temperature and moisture effects on degradation. It is notable, though, that it was only in the double-dose-treated lysimeter that chlorsulfuron concentrations decreased below the detection limit. In the single-dose lysimeter, detectable concentrations were found in leachate also during spring (as mentioned above). The different leaching patterns in the two lysimeters was most likely only a reflection of spatial variability of some parameters critical for chlorsulfuron dissipation. The effects of such spatial variability cannot easily be analysed with a model such as MACRO.

Figure 5 presents predictions of chlorsulfuron concentrations in leachate extending beyond the measurement period. All these simulations were made assuming the lower application rate ( $4 \text{ g ha}^{-1}$ ). Using the two-flow domain option, a steady decline in concentrations occurred from one leaching season (autumn/spring) to the subsequent season, throughout the 55-month simulation period (Fig. 5). In the one-flow domain mode, peak concentrations eluted during spring 1990 (two years after application: Fig. 5), reflecting the slower displacement of the herbicide through the profile when classical convective-dispersive flow behaviour was assumed. In the simulation scenario which matched the measurements (i.e. two-flow domains and a faster degradation assumed in the subsoil), chlorsulfuron concentrations were clearly below  $12.5 \text{ ng litre}^{-1}$  (the limit of detection) from autumn 1989 onwards (Fig. 5). Indeed, the concentration peak in March 1990 only reached  $0.8 \text{ ng litre}^{-1}$ .

Based on the above presentation, it is clear that non-equilibrium flow processes had a significant influence on leaching of chlorsulfuron in this particular soil. Several studies have also shown that preferential flow is a common phenomenon, not only in structured clay soils

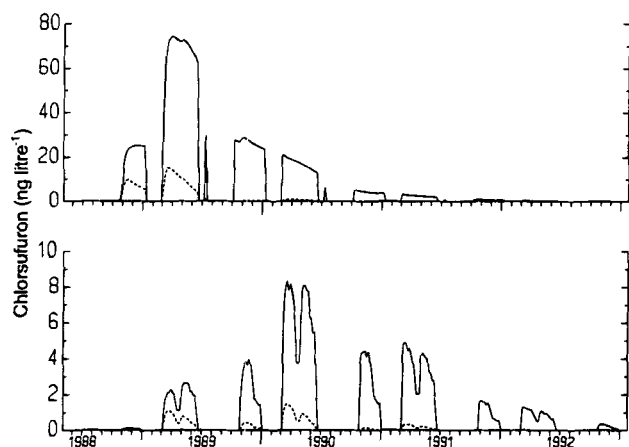


Fig. 5. Predicted chlorsulfuron concentrations in leachate, including the period extending beyond the measurement period. The upper figure shows the results of the two-flow domain simulations and the lower figure the corresponding results of the one-flow domain simulations (note the different scales on the y-axes). Solid and broken lines represent slow and fast subsoil degradation, respectively.

but also in loamy soils and structureless sands.<sup>25,26</sup> In the two-flow domain simulation (single dose and fast subsoil degradation), predicted concentrations of chlorsulfuron in the liquid phase of the two pore systems were quite different in the loamy topsoil; i.e. much higher in macropores than in micropores up until November 1989 (Fig. 6). In the sandy subsoil, concentrations were the same in both pore systems throughout the whole simulation period (Fig. 6), although considerably lower than in the topsoil. Consequently, it was the hydraulic properties of the topsoil that induced rapid bypass flow of chlorsulfuron, which caused early breakthrough of the compound in leachate. Once chlorsulfuron residues reached subsoil, the compound was transported uniformly through the soil, since the hydraulic conductivity of micropores was considerably higher than in topsoil (Table 2) and sufficiently large to maintain equilibrium flow behaviour.

### 3.3 Leaching loads of chlorsulfuron

Cumulative measured and predicted leaching loads of chlorsulfuron are summarized in Table 3. Total predicted leaching loads amounts to  $0.012$  and  $0.023 \text{ g ha}^{-1}$  in the single- and double-dose treatment, respectively, for the 11-month period for which measurements were available and for the simulations that showed good agreement with measurements. The corresponding measured values were  $0.005$  and  $0.013 \text{ g ha}^{-1}$ . These loads represent a maximum of  $0.3\%$  of the applied amount of chlorsulfuron. Considering the 55-month simulation period and, again, only the simulation that matched the measurements, the cumulative leaching load of chlorsulfuron was  $0.013 \text{ g ha}^{-1}$  when  $4 \text{ g ha}^{-1}$  of the herbicide was applied. This is only an  $8\%$  increase compared with the corresponding 11-month total. Comparing predicted leaching loads for all 55-month simulations, there was a

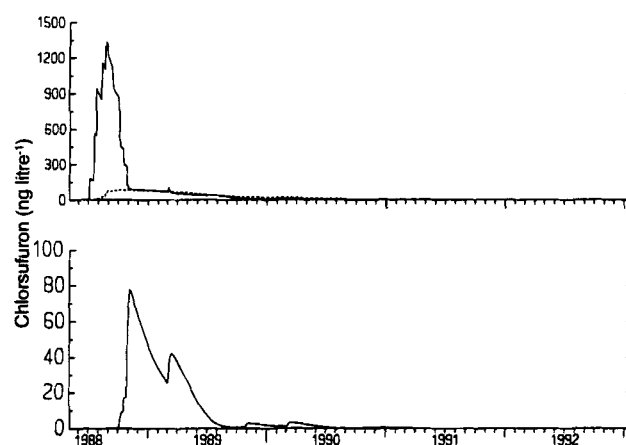


Fig. 6. Predicted chlorsulfuron concentrations in the liquid phase of macropores (solid lines) and micropores (broken lines) in a topsoil layer (18–24 cm; upper figure) and in a subsoil layer (46–54 cm; lower figure) (note the different scales on the y-axes).

TABLE 3  
Measured and Predicted Cumulative Leaching Loads of Chlorsulfuron

Dose (g AI ha <sup>-1</sup> )	Flow-domain option	Subsoil degrad. rate (day <sup>-1</sup> )	Study/simulation period (months)	Leaching load (g AI ha <sup>-1</sup> )	Leaching load (% of appl.)
<i>Measured</i>					
4		—	11	0.005	0.12
8		—	11	0.013	0.16
<i>Predicted</i>					
4	One	0.014	11	<0.001	0.02
4	One	0.07	11	<0.001	0.01
4	Two	0.014	11	0.054	1.35
4	Two	0.07	11	0.012	0.30
8	Two	0.07	11	0.023	0.29
4	One	0.014	55	0.017	0.42
4	One	0.07	55	0.002	0.05
4	Two	0.014	55	0.113	2.82
4	Two	0.07	55	0.013	0.32

tendency for subsoil degradation rates to affect leaching loads more than the alternative flow-domain options (Table 3). Slower subsoil degradation increased leaching loads by a factor of about 8.5. The corresponding factor when using the two-flow domain instead of the one-flow domain option was c.6.5. This suggests that, for this particular soil and herbicide, subsoil degradation rates (which are seldom determined) have at least as much impact on leaching loads in the long term as flow patterns.

An interesting observation regarding leaching loads of chlorsulfuron is the fact that the measured loads were considerably smaller than those predicted (Table 3), even though the measured and predicted leachate volumes and peak concentrations were similar. The main reason is that model predictions include loads calculated from pesticide concentrations below the detection limit, whereas concentrations below the detection limit were set to zero when determining the measured leached amount. In other words, it is more relevant to compare predicted and measured concentrations, rather than leaching loads, when concentrations are close to the detection limit. Bergström and Jarvis<sup>27</sup> also emphasized the importance of correctly evaluating the significance of pesticide concentrations close to the detection limit and the accompanying leaching loads. This is especially critical in the context of regulatory authorities introducing criteria for acceptable leaching losses, as is currently being discussed worldwide.

#### 4 CONCLUSIONS

Results from this study showed that the physically based dual-porosity model MACRO can be used successfully to predict very low pesticide concentrations in leachate, with a minimum of calibration. Preferential

flow was shown to be a critical process in the loamy-textured topsoil, as was degradation in subsoil layers, as well as in the topsoil. Ignoring the importance of these processes will result in poor model predictions for many soils.

Both measurements and model predictions clearly showed that chlorsulfuron concentrations below the maximum acceptable level (0.1 µg litre<sup>-1</sup> for a single pesticide in drinking water)<sup>28</sup> are to be expected in lysimeter leachate. Such chlorsulfuron concentrations would be typical for water leaving the root zone of agricultural soils. Subsequent appearance of these nondegraded, nonadsorbed pesticide residues in surface waters and groundwaters would be associated with substantial dilution to levels considerably lower than those presented here (*cf.* Reference 12).

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